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Microwave-enhanced CO_2 gasification of oil palm shell char

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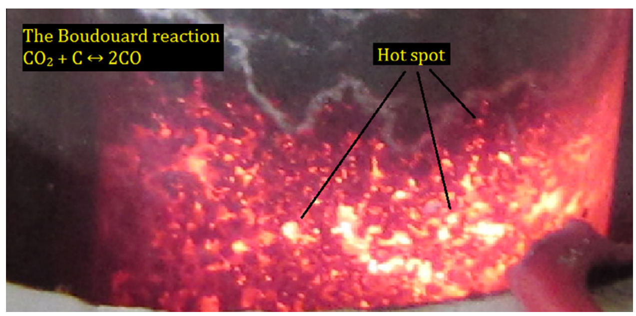
HIGHLIGHTS

- Microwave heating system was developed to convert CO_2 to CO via Boudouard reaction.
- Superior performance of microwave over thermal driven gasification was observed.
- Formation of hot spot in microwave heating pronouncedly improved char reactivity.
- E_a of 74 and 247 kJ/mol was obtained for microwave and thermal CO_2 char gasification.
- CO_2 conversion of 99% was achieved in microwave gasification of Fe-catalyzed char.

GRAPHICAL ABSTRACT



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ABSTRACT

CO_2 gasification of oil palm shell (OPS) char to produce CO through the Boudouard reaction ($C + CO_2 \leftrightarrow 2CO$) was investigated under microwave irradiation. A microwave heating system was developed to carry out the CO_2 gasification in a packed bed of OPS char. The influence of char particle size, temperature and gas flow rate on CO_2 conversion and CO evolution was considered. It was attempted to improve the reactivity of OPS char in gasification reaction through incorporation of Fe catalyst into the char skeleton. Very promising results were achieved in our experiments, where a CO_2 conversion of 99% could be maintained during 60 min microwave-induced gasification of iron-catalyzed char. When similar gasification experiments were performed in conventional electric furnace, the superior performance of microwave over thermal driven reaction was elucidated. The activation energies of 36.0, 74.2 and 247.2 kJ/mol were obtained for catalytic and non-catalytic microwave and thermal heating, respectively.

1. Introduction

Advances in microwave heating systems have opened up new avenues for prompt and effective thermal processing of materials. This emerging technology has empowered both researchers in academic communities and engineers in industry to engage in processes with reduced energy consumption and short processing time. Microwave heating systems are considered energy efficient, wherein rapid and selective material heating is achieved in only few minutes with instantaneous start-up and close-down of the processes (Kasin, 2006). Nowadays, the exploitation of microwave energy in heating applications is becoming popular due to the enhanced chemical reaction and improved yield attainable in microwave heating systems over conventional heating.

The mechanism of heating differs greatly between microwave and conventional thermal heating. Convection, conduction and radiation are the three well-known mechanisms for transfer of

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thermal energy to the heating material in conventional heating. The principle of microwave heating relies on the transformation of microwave electromagnetic energy to thermal energy throughout the entire volume of the substance which is being subjected to radiation (Will et al., 2004). Microwave heating is considered as a sub-category of dielectric heating in which, the interaction of the electric field component of electromagnetic wave with charged particles in the material (not in every material) concludes to the heating up of the material (Menendez et al., 2010). This interaction and response to the applied electric field depends on two fundamental properties of the material known as dielectric constant (ε') and dielectric loss (ε''). The dielectric constant represents the ability of the material to store the electromagnetic energy and is an indication of real permittivity. The dielectric loss is a measure of the ability of the material to dissipate the microwave energy as heat and is an indication of imaginary permittivity. These two parameters are linked together through dielectric loss tangent ($\tan \delta = \varepsilon''/\varepsilon'$) which is a measure of the ability of a material to be heated under microwave irradiation (Fernandez et al., 2011; Idris et al., 2004). A high value of $\tan \delta$ indicates a high absorbency of microwave energy.

Carbon materials are known as excellent microwave receptors with dielectric loss tangents around 0.02–2.95 (Menendez et al., 2010). The principal heating mechanism in the case of carbon and other solid materials with charge carriers (ions, electron, etc.) is explained by the movement of charged particles through a delimited region of the material under the influence of electromagnetic field which induces current. Since the charge carriers cannot couple with the phase changes of the electric field, they accumulate on the surface and dissipate energy in the form of heat. This heating mechanism is known as the interfacial or Maxwell–Wagner polarization which differs from the dipolar polarization mechanism that creates heat in polar organic-solvents and water (Menendez et al., 2010; Will et al., 2004). Considering that char and other carbonaceous materials are very good microwave absorbers, it is expected that high temperature heterogeneous gas–solid reactions would be favored under microwave irradiation.

CO_2 gasification of char, based on Boudourad reaction ($C + CO_2 \leftrightarrow 2CO$) is one of the high temperature gas-solid reactions which has long been the topic of interest, especially in the area of coal gasification. Recently, a lot of hope has been pinned on the utilization of lignocellulosic biomass residues as the source of char to carry out the Boudourad reaction. This would offer an opportunity for conversion of biomass wastes into value-added products in an environmentally benign and green manner, where the most notorious greenhouse gas, CO_2, is reduced to fuel gas, CO. Gasification of biomass-derived char with CO_2 as an evolving field of sustainability has been considered recently. Extensive studies have been conducted on the kinetics of biomass-char gasification using CO_2 (Ahmed and Gupta, 2011; Mani et al., 2011; Ollero et al., 2003) and some attempts have been made to improve the reactivity of biomass-char in CO_2 gasification reaction using catalysts (Huang et al., 2009; Lahijani et al., 2012, 2013; Mitsuoka et al., 2010). However, very few studies have focused on the implementation of microwave heating to conduct the high temperature CO_2 gasification reaction.

So far, many attempts have been made to implement microwave irradiation for pyrolysis of biomass (Abubakar et al., 2013; Huang et al., 2013; Li et al., 2013; Zhao et al., 2012); yet, little is known about microwave gasification. Menendez et al. (2006) reported some evidences of char gasification with CO_2 during the microwave induced pyrolysis of coffee hulls. Kasin (2006) patented the development of an apparatus for microwave induced pyrolysis and gasification of municipal wastes and sludge from different plants. Brzeski (2013) also published a patent regarding the development of a microwave furnace for gasification of substances to extract fuel gas. Very recently, Hunt et al. (2013) performed the CO_2 gasification of activated charcoal in microwave and discussed on the heating mechanism and thermodynamics of the reaction extensively.

This paper reports the results of an investigation specifically focused on the CO_2 gasification of biomass-derived char under microwave irradiation. To the best of authors' knowledge, similar data are very scarcely found in the open literature. In this work, oil palm shell (OPS) as an abundant lignocellulosic biomass waste in Malaysia was utilized to prepare the char. The average crude palm oil production in Malaysia was reported around 18.8 million tonnes in 2012 (www.mida.gov.my, 2012) and considering that palm shell constitutes about 6% of fresh fruit bunch, the generated OPS is estimated around 5.37 million tonnes annually. In the current investigation, the char produced from the OPS was gasified using CO_2 under microwave irradiation and the influence of char particle size, temperature and gas flow rate on the evolution of CO was considered. Moreover, it was attempted to enhance the reactivity of the char during gasification reaction through the implementation of iron-catalyzed char. To prove the salient features of microwave heating system, similar experiments were performed under conventional electric furnace heating and the results were compared. The activation energies for catalytic and non-catalytic microwave and thermal gasification reactions were calculated and compared.

2. Methods

2.1. Raw material and char preparation

Oil palm shell (OPS) was obtained from a local palm oil mill. The shells were sun dried, crushed and sieved into grains of 2–3 mm. The ground shells were washed with tap water to remove impurities then dried at 105 °C for 48 h. The ultimate analysis and proximate analysis of OPS are provided in Table 1.

The char preparation experiments were conducted in a bench scale rig designed for pyrolysis experiments. The specifications of this carbonization system have been described elsewhere (Lahijani et al., 2012). The shells were carbonized at 900 °C for 90 min to obtain OPS char. The so-obtained chars were pulverized and sieved into four different size distributions with particle diameters (d_p, in μm) of $d_p < 150$; $150 < d_p < 425$; $425 < d_p < 850$ and $d_p > 850$, using ASTM sieves, from no. 20 to 100. The ground chars were stored in desiccator.

2.2. CO_2 gasification of OPS char in microwave

The experimental set-up used to carry out the CO_2 char gasification consisted of gas cylinders (N_2 and CO_2), mass flow meters, tubular reactor packed with OPS char, microwave chamber, temperature controlling unit and gas cooling train. In order to develop a microwave heating system for gasification, a commercial microwave oven (Cornell, CMO-EL17L) with maximum output power of 1150 W and frequency of 2.45 GHz was modified to accommodate a quartz annular reactor inside the microwave cavity. The annular reactor was a double-walled quartz tube with inner and outer diameters of 1.5 and 3.5 cm and height of 30 cm. The inner tube

Table 1
The ultimate analysis and proximate analysis of OPS.

Ultimate analysis (wt%)				Proximate analysis (wt%)			
C	H	N	O[a]	Moisture	FC	Volatile	Ash
49.65	6.43	8.25	35.67	7.0	21.3	69.9	1.8

[a] By difference.